We report the results of our research activities under NREL Subcontract ADJ-2-30630-17 during the second quarter of Phase III. During this quarter we have carried out projects primarily related to the Narrow Gap Materials reporting umbrella.

We have continued to concentrate our experimental work on the characterization of the microcrystalline Si samples from United Solar Ovonics Corp. We will refer to this material as nc-Si:H. They provided us with four of these samples: Three were fabricated in a 3-layer sandwich form consisting of a 700nm thick nc-Si:H layer clad between two 200 to 250nm thick a-Si:H layers in a SS/n+/a-Si:H/nc-Si:H/a-Si:H structure upon which we deposited a semitransparent Pd Schottky barrier contact. These 3 samples were deposited with different levels of H-dilution: One was their standard (14140), one was at 25% less hydrogen (14657) and one was hydrogen profiled to keep the crystallite size more nearly constant (14661). An additional samples was a purely nc-Si:H p-i-n device containing a 1000 nm intrinsic layer in a SS/n^+/i/p^+/TCO structure. For this report we will primarily concentrate on results for the two sandwich samples: 14657 and 14661. Extensive results on the other sandwich sample, 14140, and the pin sample (12123) have been given in our previous reports.

Figure 1 compares drive-level capacitance profiling (DLCP) measurements of samples 14140 (standard hydrogen dilution) and 14661 (profiled hydrogen dilution). The profiles for the two samples appear significantly different. As we have discussed previously, under constant hydrogen dilution during growth, the DLCP density increases in the direction of film growth, exceeding 10^{16} cm^{-3} as we approach the Schottky barrier interface at the top surface of the film [see Fig. 1(a)]. This variation is believed to result from the increase in crystallite size as the film growth progresses. In contrast, the hydrogen profiled sample exhibits a DLCP profile that reaches a maximum value of about 8 x 10^{15} cm^{-3} within the middle of the film before decreasing again toward the front surface [Fig. 1(b)]. This seems to reflect the fact that, by decreasing the hydrogen dilution as growth progresses, the crystallite size reaches a maximum and then begins to decrease.

It is actually still not clear whether these DLC profiles show the concentration of deep defects within these nc-Si:H samples, or only a variation in shallow levels in the gap that are effectively acting as n-type dopants. That is, these profiles appear to be very temperature independent, and this tends to support the latter interpretation. However, this apparent variation in the effective doping density might also result from a variation in charged deep defects with energy levels lying below the quasi-Fermi level in deep depletion (i.e., below midgap). This means that we would not be able to detect their response directly using junction-based thermal emission methods like DLCP; however, they would nonetheless contribute to overall charge balance and thus lead to a change in the occupation of shallow conduction bandtail levels (or electron free carriers). This, we believe, could also account for the type of temperature independent DLCP behavior that is observed.

FIG. 1(a). Drive-level capacitance profiles for nc-Si:H sample deposited using a constant level of hydrogen dilution during film growth. Because the barrier junction is on the top surface, this implies that the profile density increases in the direction of film growth. It is believed to reflect the fact that the crystallite size also increases in this direction.
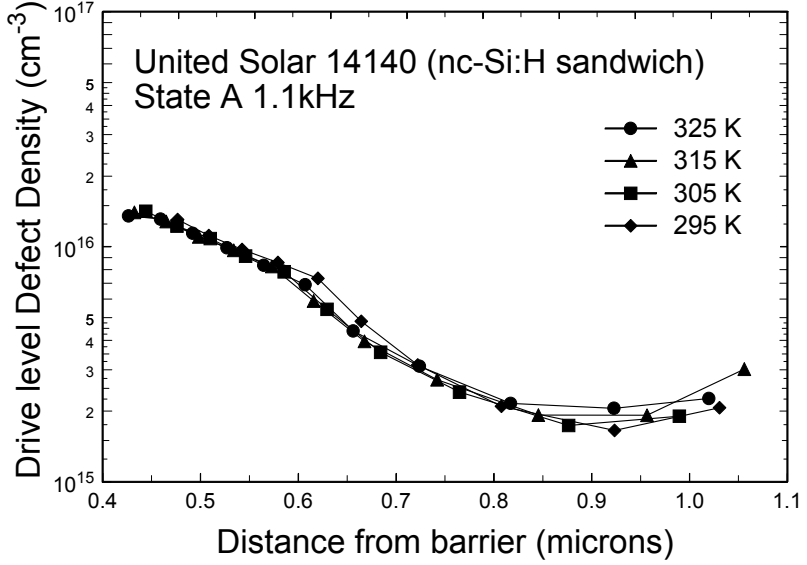

FIG. 1(b). Drive-level capacitance profiles for nc-Si:H sample deposited a varying level of hydrogen dilution during film growth. Here the profile density reaches a maximum and then decreases again as the film is deposited. This appears to reflect the fact that the crystallite size first increased but then is reduced as film growth progresses as a result of the hydrogen profiling.
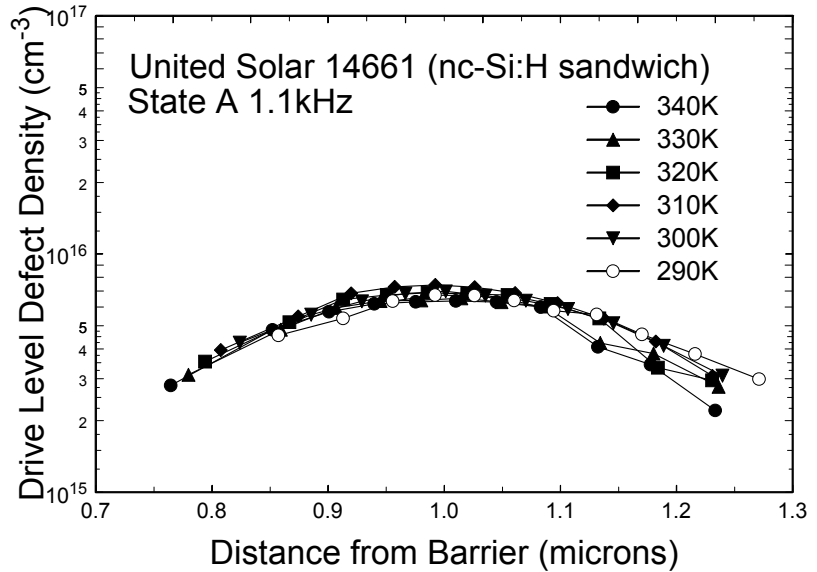

We next turn to the results of our optical spectroscopic studies of these samples. Previously we have reported results using transient photocapacitance (TPC) measurements on several of these nc-Si:H samples. Such spectra exhibit a marked temperature variation such that, at the lowest temperatures, they are nearly identical to spectra for microcrystalline Si obtained elsewhere using the CPM method [1,2,3] while, at higher temperatures, these TPC spectra appear much more similar to sub-band-gap spectra normally obtained for amorphous Si (a-Si:H). During the past quarter we have carried out TPC measurements on the hydrogen profiled sample 14461 and have found this type of temperature dependence is once again exhibited. A set of such TPC spectra for this sample device is displayed in Fig. 2(a).

A complementary measurement to that of transient photocapacitance spectroscopy is that of transient junction *photocurrent* (TPI) spectroscopy. During this past quarter we have been
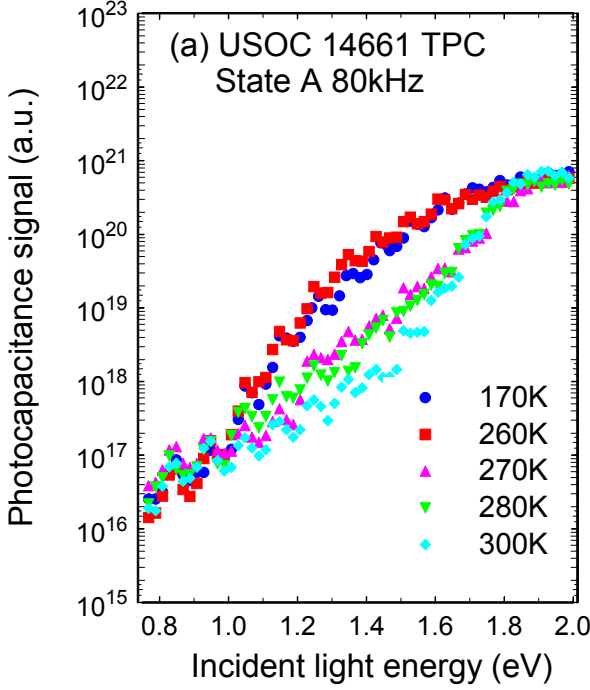
FIG. 2(a). Photocapacitance (TPC) spectra for the hydrogen profiled nc-Si:H sandwich geometry sample at several measurement temperatures. The appearance of these spectra becomes more a-Si:H like as the temperature is increased.
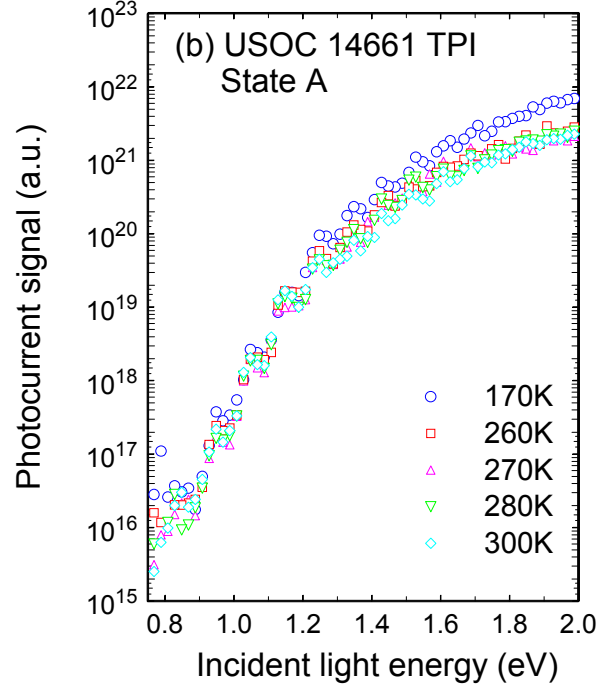
FIG. 2(b). Transient photocurrent (TPI) spectra for the same sample and measurement temperatures. Here the temperature variation is very small, and the spectra qualitatively resemble the TPC spectra taken in the lowest temperature regime.

able, for the first time, to obtain such TPI spectra on these nc-Si:H samples. A set of TPI spectra for sample 14661 is displayed in Fig. 2(b), and these have been taken at the same set of measurement temperatures as the TPC spectra shown in Fig. 2(a). Here we observe a much smaller variation with measurement temperature and, indeed, note that all of these spectra appear qualitatively similar to the lowest temperature TPC spectra.

The reason for the different appearance in these spectra is that the TPC signal results from the optically induced change of charge within the depletion region. It is thus proportional to the *difference* $n - p$ where n is the number of electrons collected and p the number of holes. Thus the TPC signal will be significantly reduced when pairs of majority and minority carriers are optically excited, and the collection fraction is similar for both carrier types. In contrast, transient photocurrent (TPI) spectroscopy looks at the time-integrated current, instead of capacitance, signal. Thus, the TPI signal is proportional to total collected carriers $n + p$. Comparisons of TPI and TPC spectra thus can determine the relative numbers of majority and minority carriers collected. This ability is unique among all the various types of sub-band-gap optical spectroscopies.

The appearance of these TPC and TPI spectra confirms the interpretation put forward in our previous reports. That is, these nc-Si:H samples are indeed predominantly micro- or nano-crystalline silicon, as indicated by the photocurrent spectra in Fig. 2(b), but they also contain a significant component of an a-Si:H phase. This phase dominates the appearance of the photocapacitance spectra at higher temperatures but does not affect the photocurrent spectra.

The reason is that the minority (hole) carrier collection coming from the nanocrystalline component in these films increases as the temperature increases and this suppresses its photocapacitance signal. Apparently, however, for the sub-band-gap transitions occurring in the a-Si:H component, a much lower fraction of the photo-excited holes are able to escape compared to the electrons. Thus, the photocapacitance signal from this component remains large even as the temperature is increased. The fact that we previously reported very similar photocapacitance spectra on the purely nc-Si:H pin sample indicates that amorphous Si is actually present as an integral component of this material itself (rather than somehow originating from the a-Si:H capping layers in the sandwich device samples). The data for sample 14661 shown in Figs. 2(a) and 2(b) would be consistent with an a-Si:H volume fraction of less than 10%.

The existence of a significant a-Si:H component in these nc-Si:H films has also recently been established from XRD and Raman spectroscopic studies.[4] It had been suspected even earlier because nc-Si:H based cells degrade with prolonged light exposure.[5] This degradation has recently been fairly convincingly directly linked to the a-Si:H component from the fact that longer wavelength light with optical energies above the gap of c-Si, but below the optical gap of a-Si:H, does not cause nc-Si:H cells to degrade.[6] Presumably, then, one would expect the degradation to be accompanied by an increase in the dangling bond deep defects within the a-Si:H component.

We have thus recently been trying to gain some insight into the degradation mechanism using the unique aspects of TPC spectroscopy to reveal the electronic properties of the individual components of these nc-Si:H films. In Fig. 3 we display TPC spectra obtained at two measurment temperatures for sample 14657 for the annealed "State A", a light-soaked "State B", as well as several partial anneal states between States B and A. The light soaked state was produced by exposure to 610nm red-filtered ELH light at an intensity of 100mW/cm^2 for 70 hours. The partial anneal states were obtained using 10 minute anneals at a series of temperatures, beginning with 380K and increasing in 20K steps. Following the 460K anneal, the original State A properties appeared to be fully restored.

The 180K TPC spectra displayed in Fig. 3(a) all appear very similar and exhibit a predominantly microcrystalline Si appearance with a distinct threshold near the c-Si bandgap of 1.1eV. They also all indicate a defect band signal below 1.0eV; however, this defect band signal does not vary in magnitude within the experimental error over this series of metastable states. Moreover, the high frequency admittance data over the same series of metastable states indicates nearly no change in capacitance or the DLCP profiles. This indicates that the electron carrier density and equilibrium Fermi level are unaffected by the light exposure and annealing treatments. One might therefore conclude that the exposure to 610nm light has not degraded the electronic properties of this nc-Si:H sample.

However, the electronic properties have indeed been degraded. This is evident from the 280K TPC spectra displayed in Fig. 3(b) which reveal definite changes as the sample is degraded and then annealed. Specifically, the microcrystalline Si appearance becomes more pronounced in the degraded state, and then the microcrystalline aspect of the spectra is monotonically reduced again after each annealing step. This means that there has been a reduction in the hole collection fraction from the nanocrystalline component due to the light-induced degradation, and this is followed by a subsequent recovery in the hole collection as the sample is annealed back toward State A.
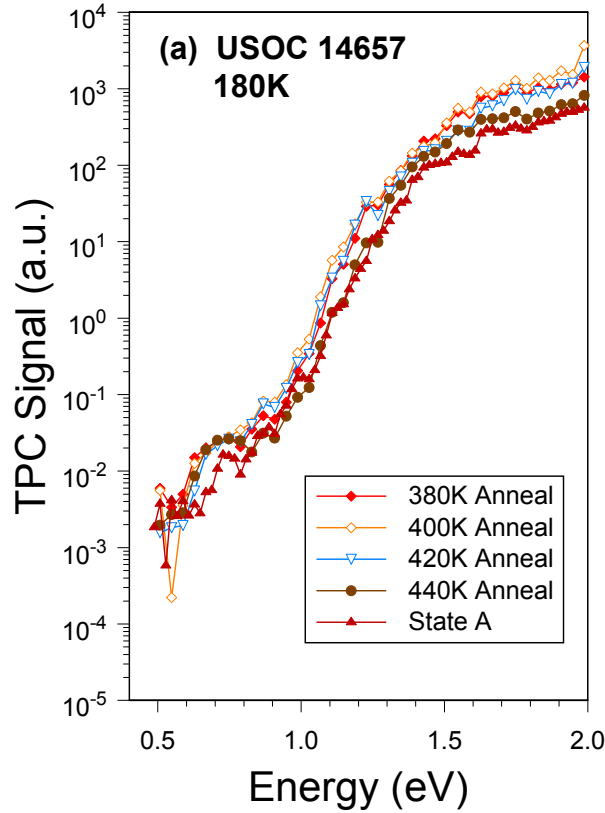
FIG. 3(a). Photocapacitance spectra for Sample 14657 taken at 180K for a series of metastable anneal states following light soaking. Because the hole collection is already significantly suppressed due to the low measurement temperature, very little change due to the degradation is visible.
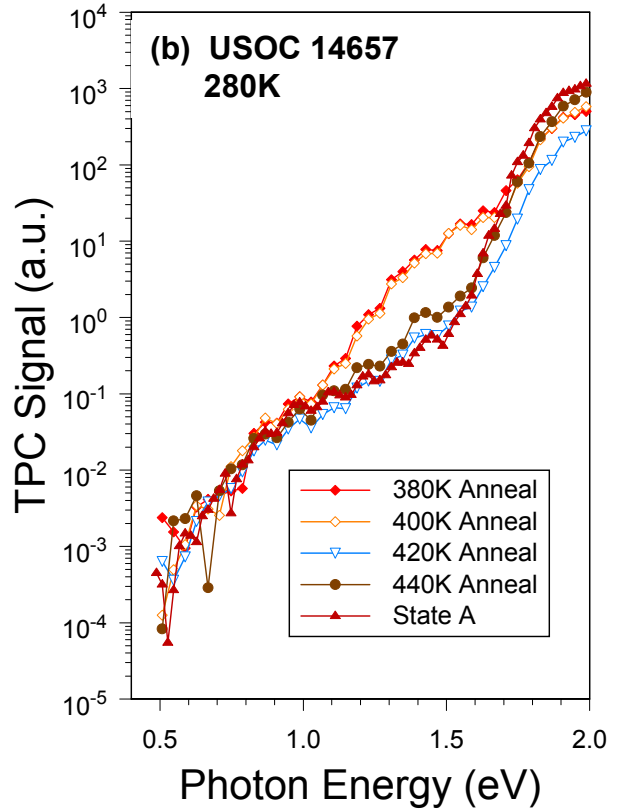
FIG. 3(b). Photocapacitance spectra for Sample 14657 taken at 280K for the same series of metastable anneal states. Here we can observe that the hole collection within the nano-crystalline component of this sample has been degraded after prolonged exposure to 610nm light.

We believe that the observed light-induced reduction in hole collection in these materials is one key factor responsible for the decrease in cell performance after degradation of nc-Si:H based cells. At the same time, our results do not reveal any increase in defects that might be responsible for this. For example, in Fig. 3(b) one can clearly discern the portion of the spectrum that corresponds to the amorphous silicon dangling bond defect band; however, this does not change within the measurement accuracy over the entire range of metastable states. Likewise, as mentioned above, the high frequency admittance is also unchanged over the full range of metastable states. Indeed, if dangling bond states were being created in the amorphous silicon portion of these samples one would expect, due to the relatively shallow Fermi level position in State A, that a considerable shift in Fermi level would occur. This, however, does *not* happen.

At present, therefore, while we can see that light-induced degradation limits the hole collection in nc-Si:H, we still have no hypothesis about how this occurs. We are currently investigating the temperature dependence of hole collection in more detail as a function of the metastable states of these samples. We thus hope to obtain some additional insight into possible mechanisms that might be responsible.

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